

Reversible Diffusion-Limited Reactions: "Chemical Equilibrium" State and the Law of Mass Action Revisited

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The validity of two fundamental concepts of classical chemical kinetics - the notion of "Chemical Equilibrium" and the "Law of Mass Action" - are re-examined for reversible *diffusion-limited* reactions (DLR), as exemplified here by association/dissociation $A + A \rightleftharpoons B$ reactions. We consider a general model of long-ranged reactions, such that any pair of A particles, separated by distance μ , may react with probability $\omega_+(\mu)$, and any B may dissociate with probability $\omega_-(\lambda)$ into a geminate pair of A s separated by distance λ . Within an exact analytical approach, we show that the asymptotic state attained by reversible DLR at $t = \infty$ is generally *not a true thermodynamic equilibrium*, but rather a non-equilibrium steady-state, and that the Law of Mass Action is invalid. The classical picture holds only in physically unrealistic case when $\omega_+(\mu) \equiv \omega_-(\mu)$ for any value of μ .

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"Chemical Equilibrium" (CE) and the "Law of Mass Action" (LMA) are two central concepts of classical chemical kinetics (see, e.g., Ref.[1]). In virtually every text-book one finds, regarding, e.g., the behavior of reversible association/dissociation reaction of the form



where K_+ and K_- are the forward and the backward rate constants, respectively, that the state achieved at $t = \infty$ is the CE. Thermodynamically, the CE is the state in which the net Gibbs free energy change of the A and B mixture vanishes. Kinetically, the CE is the state with no net change in activity, in which the rates of the forward, $K_+a_\infty^2$, and the backward, K_-b_∞ , reactions are equal and opposite, such that a_∞ and b_∞ - the A and B "equilibrium" concentrations, obey the LMA:

$$-K_+a_\infty^2 + K_-b_\infty = 0 \quad \text{or} \quad \frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} = K_{eq}, \quad (2)$$

with K_{eq} being the "equilibrium" constant, dependent on the *thermodynamic* properties only [1].

In this paper we re-examine the validity of these two fundamental concepts for reversible diffusion-limited reactions (DLR) [2]. Our objective is to determine whether for reversible DLR the CE is always a true thermodynamic equilibrium state (TES) and whether the LMA in Eq.(2) always holds. We concentrate on a simple reaction scheme in Eq.(1), but our analysis can be readily generalized (and our conclusions will remain valid) for any other type of reversible DLR. We consider a general reaction model with long-ranged reaction probabilities: That is, any pair of randomly moving A s, separated by distance

μ , may associate with probability $\omega_+(\mu)$, while any product molecule B may dissociate spontaneously producing, with probability $\omega_-(\lambda)$, a geminate pair of A s separated by distance λ . For this model, in terms of a formally exact approach, we deduce a criterion determining when the classical LMA in Eq.(2) holds and when the asymptotic $t = \infty$ state is a true TES. We show that this is only the case when $\omega_+(\mu) \equiv \omega_-(\mu)$ for any μ , which is apparently a non-realistic condition. On contrary, when the bimolecular forward and the unimolecular backward reaction probabilities do not coincide exactly, (which is more appropriate on physical grounds), we find that the LMA in Eq.(2) is violated and that the CE is not a true TES but rather a nonequilibrium steady-state. This finding is, of course, in a striking contradiction with the generally accepted classical picture.

The classical picture was, however, already shown to be inadequate in many situations. For example, for reversible reactions it predicts an exponential approach toward the CE state. It was realized that this is not the case for reversible DLR; here, the concentrations approach the asymptotic $t = \infty$ state only as a power law ($t^{-d/2}$ in d dimensions) [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. This *anomalous* behavior, which stems out of many particle and non-linear effects, was indeed observed in excited state proton transfer reactions [14].

For the reversible DLR the validity of LMA in Eq.(2) was questioned in Refs.[3] and [6], where some non-vanishing corrections were obtained within *approximate* approaches. On contrary, *exact solutions* obtained in Refs.[11] and [13] in *contact reaction* approximation, have shown that the LMA holds and that the CE state is a true TES. Note, however, that *contact reaction* approximation is just a mathematical trick employed to obtain a

tractable formalism at expense of a large degree of arbitrariness especially regarding the choice of the "reaction radius". In reality, an elementary reaction act results from an interplay of many factors and is influenced by solvent structure, potential interactions, a variety of particles' energies and angular orientations, quantum processes of different origin and etc [15], such that the reaction constants are actually long-ranged and the very notion of a fixed "reaction radius" does not make much sense. To elucidate such a delicate issue as the nature of the asymptotic $t = \infty$ state, (and to reconcile the discord between Refs.[3, 6] and [11, 13]), one has to consider the realistic distance-dependent reaction probabilities, which has not been done so far within a rigorous approach.

Consider a d -dimensional hypercubic lattice of spacing ℓ , containing A and B particles, which perform unconstrained random walks between neighboring sites. At any time moment t , any two A s may react with prob-

ability $\omega_+(\mu)$, where μ is an instantaneous distance between these A s, and form a B particle, placed at the half-distance between two A s. Any B , in turn, may dissociate with probability $\omega_-(\lambda)$ producing a randomly oriented pair of A s separated by distance λ . The long-ranged reaction constants are: $k_+(\mu) = k_+\omega_+(\mu)$ and $k_-(\lambda) = k_-\omega_-(\lambda)$, where k_+ and k_- are some amplitudes. The overall constants are thus given by $K_+ = \sum_\mu k_+(\mu)$ and $K_- = \sum_\lambda k_-(\lambda)$. We suppose that $k_+(\mu)$ and $k_-(\lambda)$ are *arbitrary* summable functions of μ and λ .

The state of the system is determined by time- and site-dependent occupation numbers $A(x)$ and $B(x)$. Let $P_t[A, B]$ denote the probability of finding the system in configuration $A = \{A(x)\}$ and $B = \{B(x)\}$ at time moment t . The time evolution of $P_t[A, B]$ due to reactions and diffusion processes on the microscopic, many particle level is governed by the following master equation:

$$\begin{aligned} \dot{P}_t[A, B] = & \frac{D}{\ell^2} \sum_x \sum_{e_x} \left[\left(A(e_x) + 1 \right) P_t[A(x) - 1, A(e_x) + 1, B] + \left(B(e_x) + 1 \right) P_t[A, B(x) - 1, B(e_x) + 1] \right. \\ & - \left. \left(A(x) + B(x) \right) P_t[A, B] \right] + \sum_\mu k_+(\mu) \sum_x \left[\left(A(x - \frac{\mu}{2}) + 1 \right) \left(A(x + \frac{\mu}{2}) + 1 \right) \times \right. \\ & \times \left. P_t[A(x - \frac{\mu}{2}) + 1, A(x + \frac{\mu}{2}) + 1, B(x) - 1] - A(x - \frac{\mu}{2}) A(x + \frac{\mu}{2}) P_t[A, B] \right] \\ & + \sum_\lambda k_-(\lambda) \sum_x \left[\left(B(x) + 1 \right) P_t[A(x - \frac{\lambda}{2}) - 1, A(x + \frac{\lambda}{2}) - 1, B(x) + 1] - B(x) P_t[A, B] \right] \end{aligned} \quad (3)$$

where $D = \ell^2/2d\tau$ is A and B particles diffusion coefficient, τ is a hopping time, while \sum_{e_x} denotes summation over orientations of the lattice vector e_x .

Our analytical approach to the solution of Eq.(3) is based on formally exact Poisson representation method, proposed originally in Ref.[16] for systems without diffusion, and elegantly generalized in Ref.[13] for reversible DLR in contact approximation. Extension of this approach to long-ranged reversible DLR is straightforward and here we merely outline the steps involved.

Our next step consists in projecting $A(x)$ and $B(x)$ onto the Poisson states $\alpha = \{\alpha(x)\}$ and $\beta = \{\beta(x)\}$ [16]:

$$\begin{aligned} P_t[A, B] = & \int \prod_x d\alpha(x) d\beta(x) \frac{\exp(-\alpha(x)) \alpha(x)^{A(x)}}{A(x)!} \times \\ & \times \frac{\exp(-\beta(x)) \beta(x)^{B(x)}}{B(x)!} F_t[\alpha, \beta], \end{aligned} \quad (4)$$

which results, after some straightforward calculations, in

the following Fokker-Planck equation for $F_t[\alpha, \beta]$:

$$\begin{aligned} \dot{F} = & \sum_x \left\{ \frac{1}{2} \frac{\partial^2 (C_2 F)}{\partial \alpha(x - \frac{\mu}{2}) \partial \alpha(x + \frac{\mu}{2})} - \right. \\ & - \frac{\partial (C_1 F)}{\partial \alpha(x)} - \frac{\partial (C_2 F)}{\partial \beta(x)} + \\ & + \left. \frac{D}{\ell^2} \left[\frac{\partial}{\partial \alpha(x)} (\Delta \alpha(x) F) + \frac{\partial}{\partial \beta(x)} (\Delta \beta(x) F) \right] \right\}, \end{aligned} \quad (5)$$

where Δ is the second finite difference operator, and

$$\begin{aligned} C_1 = & - \sum_\mu k_+(\mu) \alpha(x) \left(\alpha(x - \mu) + \alpha(x + \mu) \right) + \\ & + \sum_\mu k_-(\mu) \left(\beta(x - \mu) + \beta(x + \mu) \right), \quad (6) \\ C_2 = & \sum_\mu \left(k_+(\mu) \alpha(x + \frac{\mu}{2}) \alpha(x - \frac{\mu}{2}) - k_-(\mu) \beta(x) \right) \quad (7) \end{aligned}$$

Using Itô's equivalence, we find next the following non-

linear Langevin equations corresponding to Eq.(5):

$$\begin{cases} \dot{\alpha}(x) - D\Delta\alpha(x) = C_1 + \zeta(x, t), \\ \dot{\beta}(x) - D\Delta\beta(x) = C_2, \end{cases} \quad (8)$$

where $\zeta(x, t)$ is a Gaussian noise with zero mean and

$$\begin{aligned} \langle \zeta(x, t) \zeta(x + x', t') \rangle &= \delta(t - t') [k_-(x') \langle \beta(x') \rangle \\ &- k_+(x') \langle \alpha(x - x'/2) \alpha(x + x'/2) \rangle]. \end{aligned} \quad (9)$$

Taking into account that $\langle \alpha(x) \rangle = a_t$ and $\langle \beta(x) \rangle = b_t$ [16], where a_t and b_t are A and B particles' mean concentrations, we represent the Poisson fields as the sum of mean values and fluctuations, such that

$$\begin{aligned} \alpha(x) &= a_t + \delta\alpha(x, t), \\ \beta(x) &= b_t + \delta\beta(x, t) \end{aligned} \quad (10)$$

Substituting next these expressions into Langevin Eqs.(8) and averaging, we find that a_t and b_t follow:

$$\dot{a}_t = -2K_+ a_t^2 + 2K_- b_t + 2\Omega_t(p=0), \quad \dot{b}_t = -2\dot{a}_t, \quad (11)$$

where

$$\Omega_t(p) \equiv - \int d\mu e^{i(\mu \cdot p)} k_+(\mu) \sigma_{\alpha\alpha}(\mu, t), \quad (12)$$

and $\sigma_{\alpha\alpha}(\mu, t)$ is the pairwise correlation function:

$$\sigma_{\alpha\alpha}(\mu, t) = \langle \delta\alpha(x - \mu/2, t) \delta\alpha(x + \mu/2, t) \rangle. \quad (13)$$

Equations (11) are formally exact for any t and show that the time evolution of observables a_t and b_t is coupled to that of correlations. For $t = \infty$, we get from Eqs.(11):

$$\frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} + \frac{\Omega_\infty(0)}{K_+ b_\infty}, \quad (14)$$

which resembles the classical LMA in Eq.(2), but differs from it due to the term $\Omega_\infty(0)/K_+ b_\infty$, which embodies all non-trivial physics associated with fluctuation effects; the classical LMA holds if and only if $\sigma_{\alpha\alpha}(\mu, \infty) \equiv 0$.

Hence, we focus on $\sigma_{\alpha\alpha}(\mu, \infty)$. From Eqs.(8) we have that the Fourier-transformed $\sigma_{\alpha\alpha}(\mu, t)$ follows

$$\begin{aligned} \sigma_{\alpha\alpha}(p, t) &= \left\langle \left[G_{\alpha\beta}(p, t) * \left(C_2(p) + \delta\beta_0(p) \delta(t) \right) \right]^2 \right\rangle \\ &+ \left\langle \left[G_{\alpha\alpha}(p, t) * \left(C_1(p) + \zeta(p, t) + \delta\alpha_0(p) \delta(t) \right) \right]^2 \right\rangle \\ &+ 2 \left\langle \left[G_{\alpha\alpha}(p, t) * \left(C_1(p) + \zeta(p, t) + \delta\alpha_0(p) \delta(t) \right) \right] \right. \\ &\times \left. \left[G_{\alpha\beta}(p, t) * \left(C_2(p) + \delta\beta_0(p) \delta(t) \right) \right] \right\rangle, \end{aligned} \quad (15)$$

where " $*$ " denotes the time convolution, while $\delta\alpha_0$ and $\delta\beta_0$ stand for the initial values of the Fourier-transformed fluctuations. Note, however, that the latter produce exponentially decreasing with t terms and hence, are insignificant. In turn, the propagator $G(p, t)$ is an inverse

of the matrix $M(p, t)$, $G(p, t) = M^{-1}(p, t)$, which is defined in the Fourier-Laplace space as:

$$\begin{pmatrix} s + Dp^2 + 2a_\infty(K_+ + k_+(p)) & -2k_-(p) \\ -2a_\infty k_+(p) & s + Dp^2 + K_- \end{pmatrix}, \quad (16)$$

$k_\pm(p)$ being the Fourier-transformed reaction constants.

We proceed further with a diagrammatic expansion of Eq.(15), which has been previously developed in Ref.[11] for *contact* DLR, and represents an expansion with respect to deviations from the equilibrium situation in Eq.(2). In our case of long-range DLR, it can be deemed as an expansion in powers of a small parameter:

$$\epsilon(p) = k_+(p) a_\infty^2 - k_-(p) b_\infty. \quad (17)$$

In doing so, we obtain, in the linear order in $\epsilon(p)$, the following integral equation for $\sigma_{\alpha\alpha}(p, \infty)$:

$$\sigma_{\alpha\alpha}(p, \infty) = \left[\Omega_\infty(p) - \epsilon(p) \right] \int_0^\infty dt G_{\alpha\alpha}^0(p, t)^2, \quad (18)$$

where $G_{\alpha\alpha}^0(p, t)$ is the corresponding propagator:

$$G_{\alpha\alpha}^0(p, t) = \sum_{\gamma=\pm} \frac{(K_- - q^\gamma)}{q^+ - q^-} e^{-(Dp^2 + q^\gamma)t}, \quad (19)$$

with

$$q^\pm = \left[K_- + 2a_\infty K_+ (1 + w_+(p)) \pm \sqrt{q} \right] / 2, \quad (20)$$

$$\begin{aligned} q &= \left[K_- + 2a_\infty K_+ (1 + w_+(p)) \right]^2 - \\ &- 16K_+ K_- a_\infty (1 - w_+(p)) \left(\frac{1}{2} + w_+(p) \right). \end{aligned} \quad (21)$$

Now we are in position to deduce a criterion showing when the LMA in Eq.(2) is violated already in the linear order. To do this, we have to define from Eq.(18) conditions when $\sigma_{\alpha\alpha}(p, \infty) \neq 0$. Suppose, on contrary, that $\sigma_{\alpha\alpha}(p, \infty) \equiv 0$. This implies, in virtue of Eq.(12), that $\Omega_\infty(p) \equiv 0$. Hence, in order to have $\sigma_{\alpha\alpha}(p, \infty) \equiv 0$, the parameter $\epsilon(p)$ in Eq.(17) should be equal to zero. i.e.,

$$k_-(p) b_\infty \equiv k_+(p) a_\infty^2 \quad \text{for any } p, \quad (22)$$

or, in the μ -domain, the equality $k_-(\mu) b_\infty \equiv k_+(\mu) a_\infty^2$ should hold for any μ . One infers then that the identity in Eq.(22) may hold only if the reaction probabilities obey: $\omega_-(\mu) \equiv \omega_+(\mu) = \omega(\mu)$ for any μ , i.e. the elementary reactions are *microscopically homogeneous*. We note that Refs.[11] and [13], which predicted that the classical LMA holds and that the CE is a true TES, focused precisely on the case of *microscopically homogeneous* contact reactions with $\omega(\mu) = \delta(\mu)$. If, on contrary, the elementary reactions are *microscopically inhomogeneous*, i.e., $\omega_-(\mu) \neq \omega_+(\mu)$, pair correlations $\sigma_{\alpha\alpha}(\mu, \infty) \neq 0$, and hence, the LMA in Eq.(2) is violated. Therefore, general conclusions of Refs.[3] and [6], which analyzed

microscopically inhomogeneous reactions using approximate approaches, are also qualitatively correct.

Note now that, remarkably, the violation of the LMA implies that the corresponding "Chemical Equilibrium" is not a true TES. This can be readily understood if one notices that already in the linear order $G(p, t)$ is dependent on particles diffusion coefficient D , (see Eq.(19)). This implies that for *microscopically inhomogeneous* reactions, $\sigma_{\alpha\alpha}(\mu, \infty)$ does depend on such "kinetic" parameter as D , which means, in turn, that the CE is not a true TES but rather a non-equilibrium steady-state.

To illustrate our general conclusions we focus now on 3D systems with exponential $k_+(\mu)$ and $k_-(\lambda)$:

$$k_+(\mu) = \frac{K_+}{8\pi R^3} e^{-|\mu|/R} \quad \text{and} \quad k_-(\lambda) = \frac{K_-}{8\pi \Lambda^3} e^{-|\lambda|/\Lambda}. \quad (23)$$

In this case, we find from Eq.(18) that a_∞ and b_∞ obey:

$$\frac{a_\infty^2}{b_\infty} = \frac{K_-}{K_+} \left[1 + \frac{K_+}{16\pi D R} \left(1 - \frac{R}{\Lambda} \right) + \mathcal{O}\left((\Lambda - R)^2\right) \right], \quad (24)$$

which holds for sufficiently small R and Λ . Eq.(24) also signifies that a_∞ and b_∞ depend on D , which dependence fades out when either $D \rightarrow \infty$ or $R = \Lambda$. As well, we find that the large- μ behavior of pair correlations follows:

$$\sigma_{\alpha\alpha}(\mu, \infty) \approx \frac{16b_\infty a_\infty^2 K_- K_+^2 (\Lambda^2 - R^2)}{4\pi D^2 (4K_+ a_\infty + K_-)} \frac{e^{-\mu/\Lambda_{corr}}}{\mu}, \quad (25)$$

where the correlation length Λ_{corr} is also D -dependent:

$$\Lambda_{corr} = \sqrt{\frac{D}{4K_+ a_\infty + K_-}}. \quad (26)$$

Note that Λ_{corr} may be much greater than R , Eq.(23), when $\tau_{chem} = (4K_+ a_\infty + K_-)^{-1} \gg \tau_{diff} = R^2/D$, which is a fingerprint of an essentially cooperative behavior.

In conclusion, we re-examined the validity of two fundamental concepts of classical chemical kinetics - the notion of "Chemical Equilibrium" and the "Law of Mass Action" - on example of diffusion-limited reversible $A + A \rightleftharpoons B$ reactions with general, distance-dependent reaction probabilities. In terms of a formally exact approach based on Gardiner's Poisson representation method [16], we deduced a criterion determining the conditions when the classical LMA holds and when the CE is a true TES. We realized that this is the case only when the elementary reaction probabilities obey the condition of *microscopic homogeneity*: $\omega_+(\mu) \equiv \omega_-(\mu)$ for any μ , which is apparently unrealistic since the *bimolecular* forward and *unimolecular* backward reactions are supported by completely different physical processes of classical and quantum origin. On contrary, we found that for *microscopically inhomogeneous* reactions, when $\omega_+(\mu) \neq \omega_-(\mu)$,

the classical LMA is violated and the CE is not a true TES but rather a nonequilibrium steady-state.

Consequently, for reversible DLR the diffusional relaxation of the system is not fast enough to offset the perturbative effect of ongoing *microscopically inhomogeneous* elementary reactions even in the asymptotic $t = \infty$ state. We emphasize that such a non-equilibrium steady-state is observed for a *closed* system with the *conserved* overall concentration of particles, without any external inflow of particles. We also note that contrary to the dynamical behavior of reversible DLR, (for which an anomalous power-law decay emerges if some *conservation laws* are present [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]), for *microscopically inhomogeneous* reactions the LMA would be evidently violated and the CE would be a non-equilibrium steady-state also in *absence* of conserved parameters. We finally remark that the DLR furnish a remarkable example of systems, for which an arbitrarily small but finite difference (of classical or quantum origin) between the microscopic rates $\omega_+(\mu)$ and $\omega_-(\mu)$ results in a fundamental change in the macroscopic asymptotic $t = \infty$ behavior.

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